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Radiochemical analysis of 41Ca, 90Sr, 129I and 36Cl in waste samples

Hou, Xiaolin

Publication date:
2009

Radiochemical analysis of ^{41}Ca, ^{90}Sr, ^{129}I and ^{36}Cl in waste samples

Xiaolin Hou

Risø National Laboratory for Sustainable Energy ,
Technical University of Denmark

Main Radionuclides in the nuclear waste and used materials in the view of measurement

- Gamma radionuclides

  ^{60}Co, ^{133}Ba, ^{137}Cs, ^{134}Cs, ^{106}Ru, $^{152,154,155}Eu$, ^{58}Co, ^{54}Mn, ^{59}Fe, ^{110m}Ag, ^{94}Nb.

- Beta Emitter

  ^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, $^{63,59}Ni$, ^{93}Zr, ^{93}Mo, ^{90}Sr, ^{99}Tc, ^{129}I.

- Alpha emitter (transuanics)

  $^{238-241}Pu$, ^{241}Am, $^{243,244}Cm$, ^{237}Np

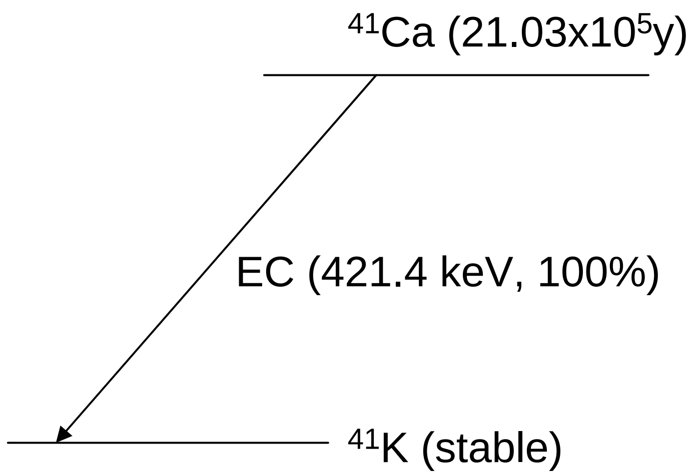
Waste samples and the relevant critical radionuclides for decommissioning

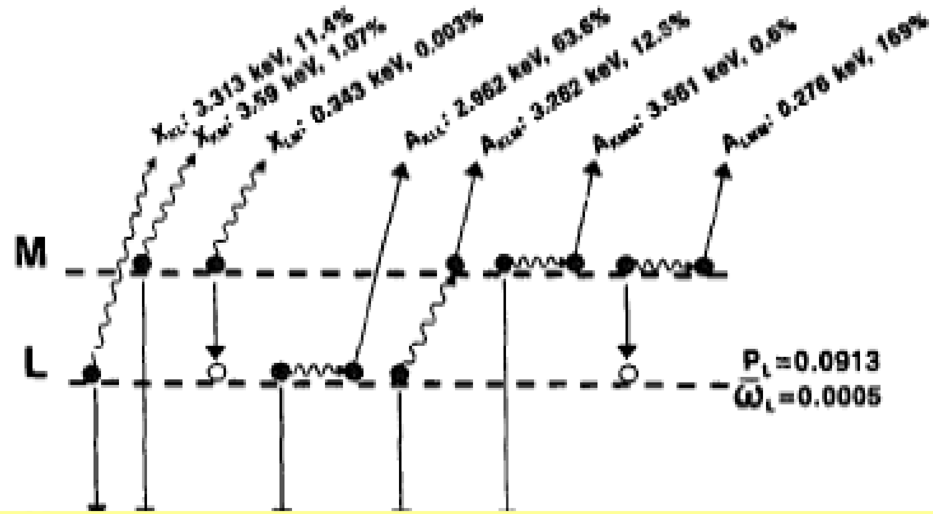
- Graphite (reactor)
  - ^{3}H, ^{14}C, ^{55}Fe, $^{63, 59}Ni$, ^{60}Co, ^{152}Eu
- Concrete (normal or heavy)
  - ^{41}Ca, ^{60}Co, ^{55}Fe, $^{63, 59}Ni$, ^{133}Ba, ^{152}Eu
- Steel/stainless steel
  - ^{55}Fe, $^{63, 59}Ni$, ^{36}Cl, ^{93}Zr, ^{93}Mo, ^{94}Nb, ^{60}Co, ^{152}Eu, transuranics
- Aluminium
  - ^{60}Co, ^{63}Ni, ^{55}Fe, ^{36}Cl
- Lead
  - , ^{60}Co, ^{63}Ni, ^{55}Fe
- Water
  - ^{3}H, ^{14}C, ^{63}Ni, ^{99}Tc, ^{129}I, ^{90}Sr, ^{60}Co, ^{137}Cs, transuranics
- Ion exchange resin
  - ^{55}Fe, $^{63,59}Ni$, ^{14}C, ^{99}Tc, ^{36}Cl, ^{93}Zr, ^{93}Mo, ^{94}Nb ^{90}Sr, ^{129}I, ^{137}Cs, ^{60}Co, ^{135}Cs, transuranics

^{41}Ca in the concrete

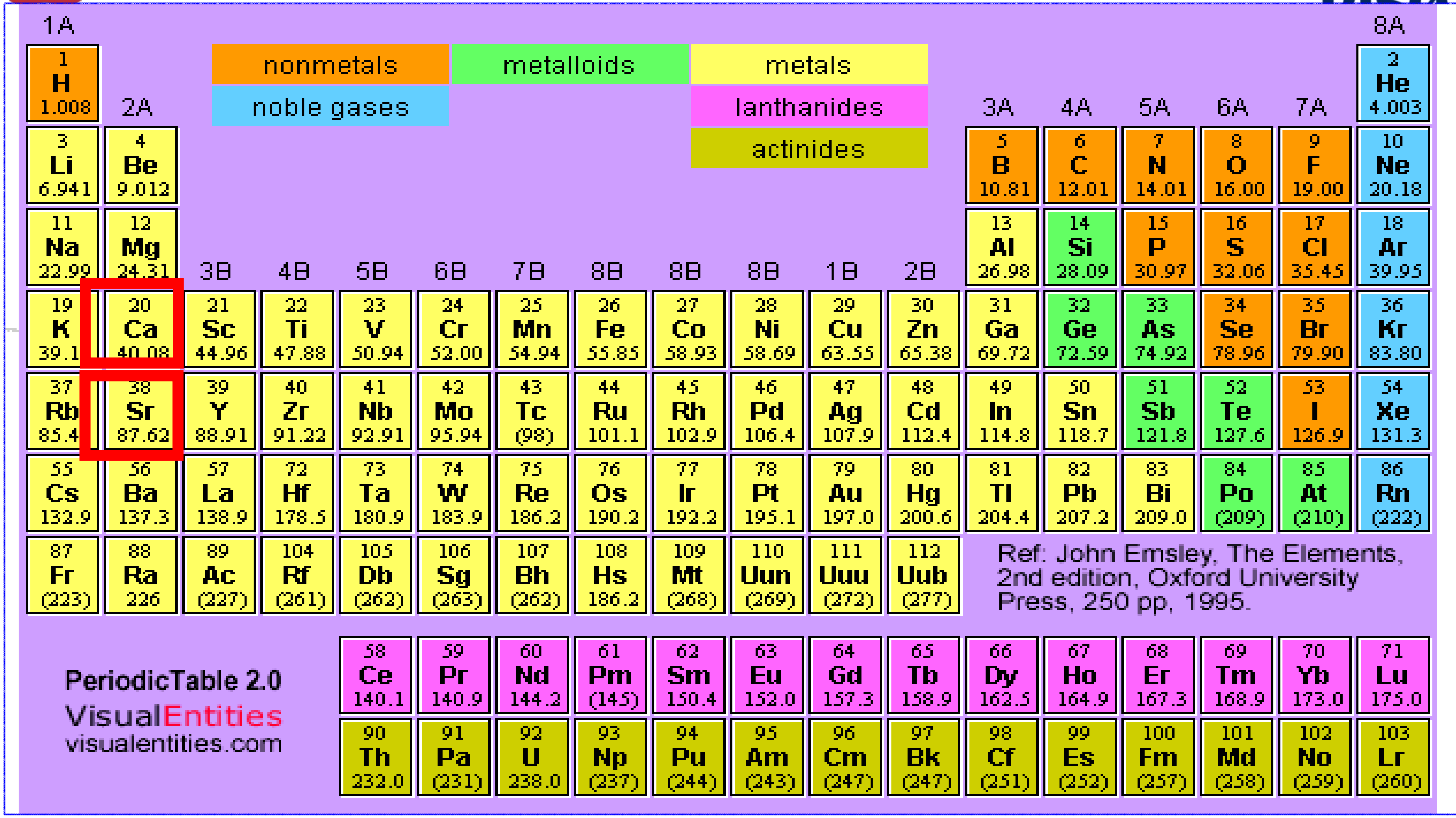
Activation products of calcium isotopes

Nuclide	Target isotope Aboundance %	Reaction	Cross section, bar	Half life	Decay
^{41}Ca	96.94	$^{40}Ca(n, \gamma)^{41}Ca$	0.41	1.03×10^{5} y	EC
^{45}Ca	2.086	$^{44}Ca(n, \gamma)^{45}Ca$	0.84	162.7 d	β-
^{47}Ca	0.004	$^{46}Ca(n, \gamma)^{47}Ca$	0.7	4.54 d	β, γ
^{49}Ca	0.187	$^{48}Ca(n, \gamma)^{49}Ca$	1.0	8.72 min.	β, γ





Energy of X-rays and Auger electrons : 0.3-3.6 keV
Determination: X-ray spectrometry (<0.08%)
LSC (10-20%)



Sr & Ca: Alkline earth element

Determination ^{41}Ca in concrete

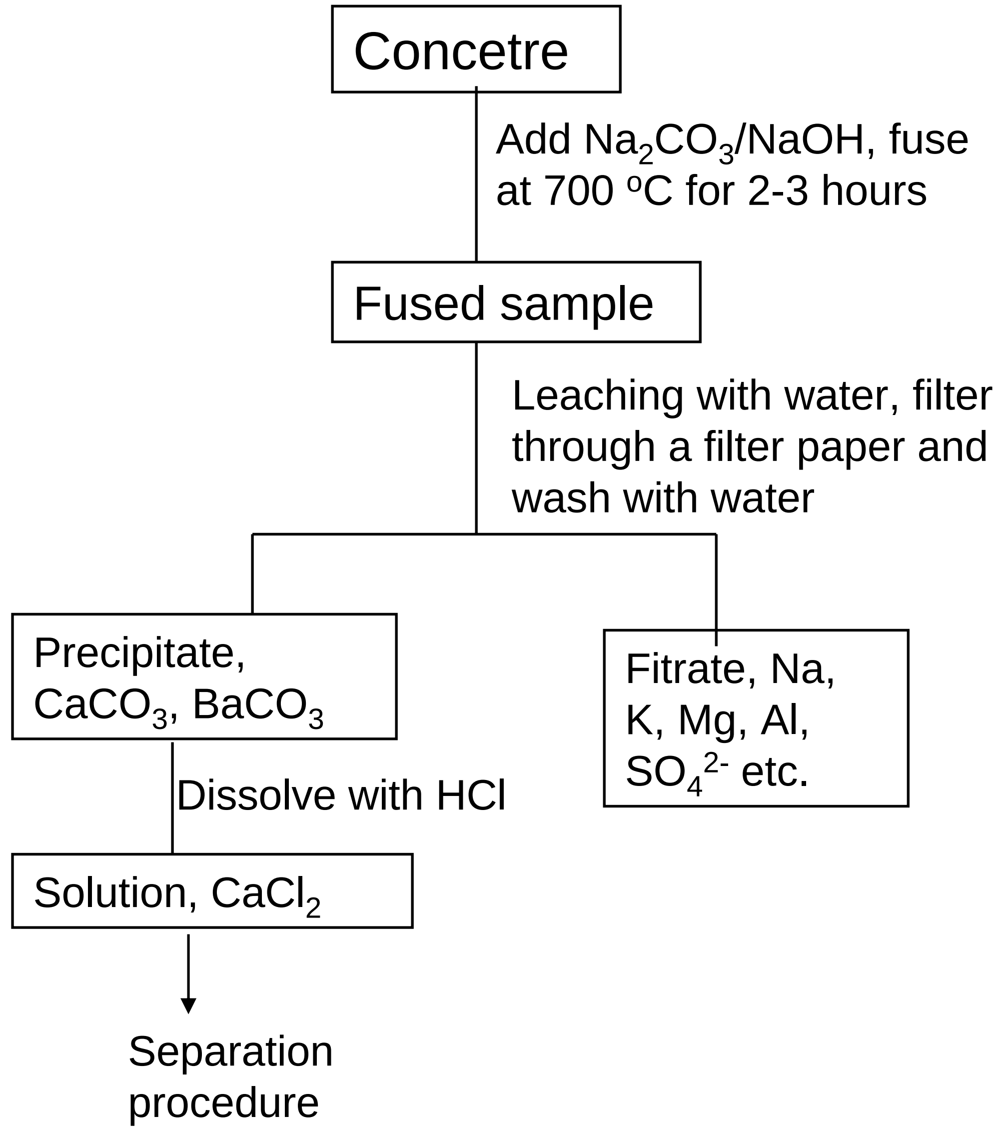
- Separation fro matrix
  - Decomposition of heavy concrete by alkali fussion
  - Leaching Ca by acids
- Separation from active metals such as ^{60}Co, ^{152}Eu, ^{55}Fe, ^{63}Ni, ^{65}Zn, ^{54}Mn, ^{51}Cr,etc.
  - Precipitation with $Fe(OH)_3$ by hydroxides at pH9
- Separation from other alkaline metals, such as ^{133}Ba, ^{226}Ra and ^{90}Sr.
  - $BaCrO_4$ and $SrCrO_4$ precipitation
  - $BaCl_2$ and $SrCl_2$ precipitation in HCl solution
  - $Ca(OH)_2$ precipitation in NaOH solution

Concrete in the reactor

- Ordinary concrete
- Heavy concrete (50-70% $BaSO_4$ was added)

Decomposition of concrete for ^{41}Ca and other radionuclides

- For Ordinary concrete, silicates of calcium does not easily be decomposed by acids
- For heavy concrete, some calcium exists as $CaSO_4$, which does not dissolved by acid.
- Alkaline fusion have to be used for the decomposition of concrete for the determination of calcium isotopes.



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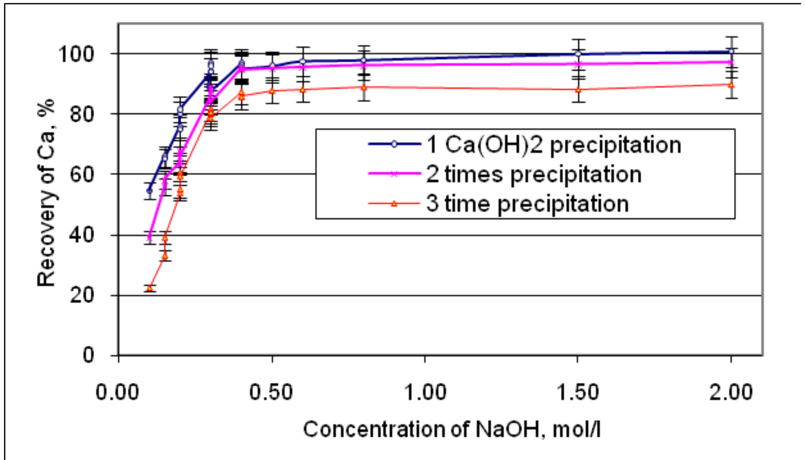
Separation of Ca and Sr from other metals by hydroxides precipitation followed by carbonate precipitation

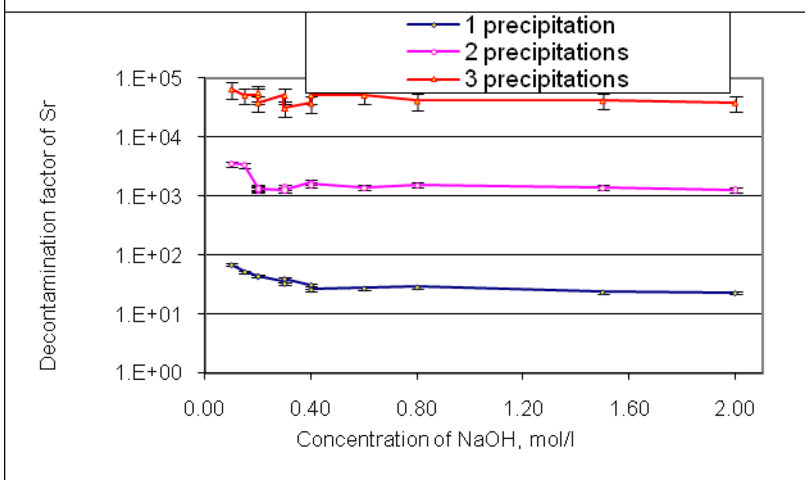
Element /nuclide	Recovery, %	Element / nuclide	Decontamination factor
Ca	97.7±3.9	^{137}Cs	$(4.5\pm0.3)\times10^5$
^{85}Sr	97.9±2.1	^{60}Co	$(1.2\pm0.4)\times10^5$
^{133}Ba	97.3±2.8	^{152}Eu	$(8.5\pm0.5)\times10^5$
		^{59}Fe	$(2.5\pm0.1)\times10^5$
		^{63}Ni	$(2.5\pm0.2)\times10^5$

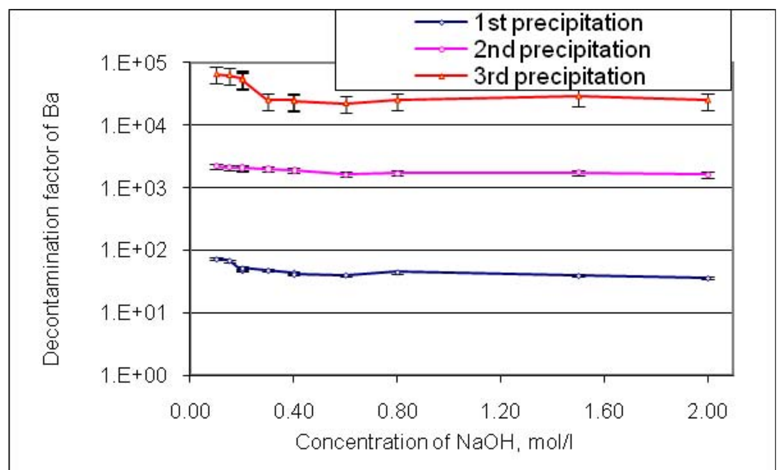
The new method for the separation of Ca from Sr and Ba

- Separation of Sr from Ca by $Ca(OH)_2$ precipitation
  - $Ca(OH)_2$: insoluble, Ksp = 5.2×10^{-6}
  - $Sr(OH)_2$ and $Ba(OH)_2$: Soluble in alkine solution



Precipitate Ca as $Ca(OH)_2$ at 0.5 – 0.8 mol/l NaOH, repeat 3 times, 85% Ca can be recovered, and the decontamination factor for Sr and Ba are higer than 5×10^4





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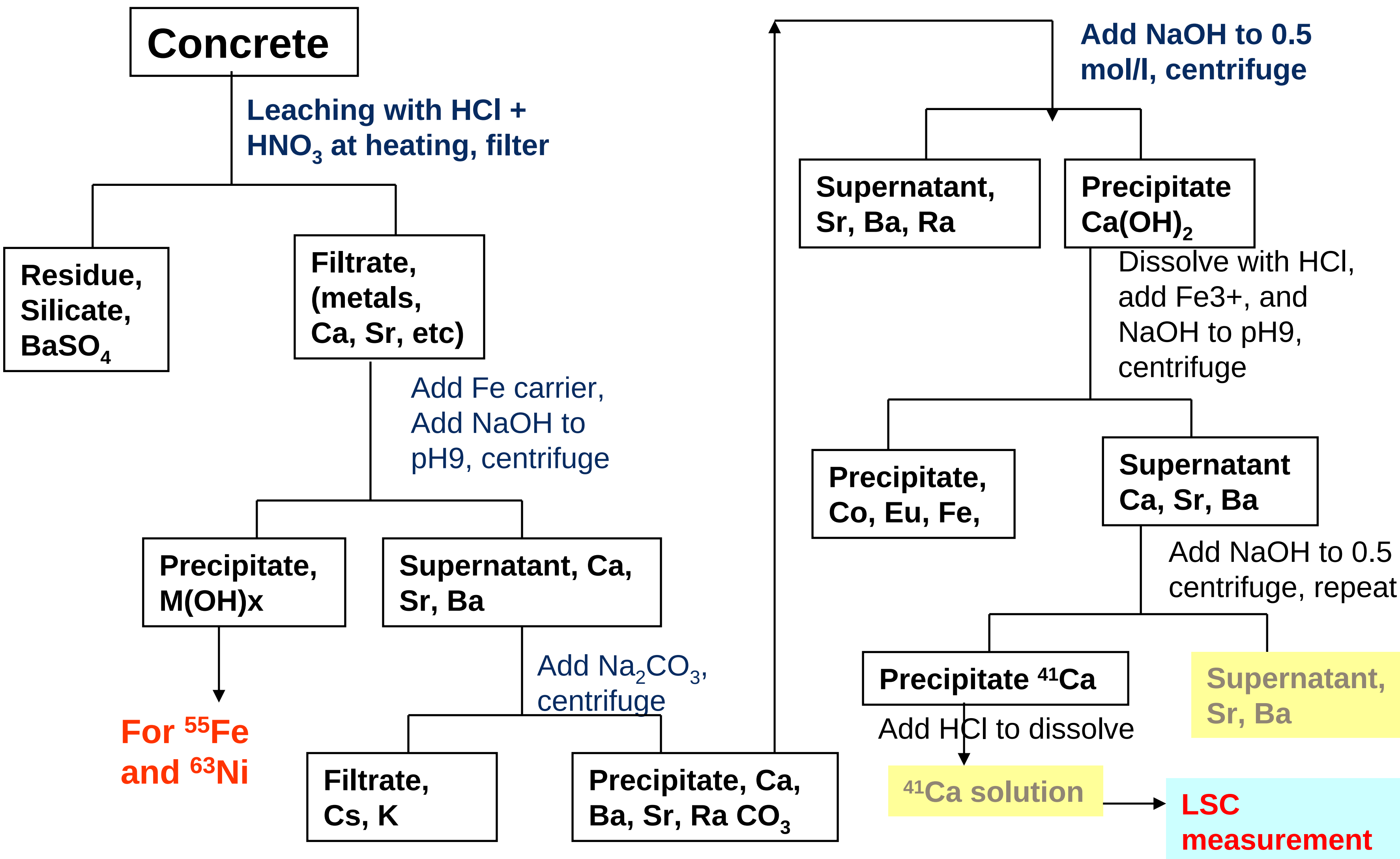
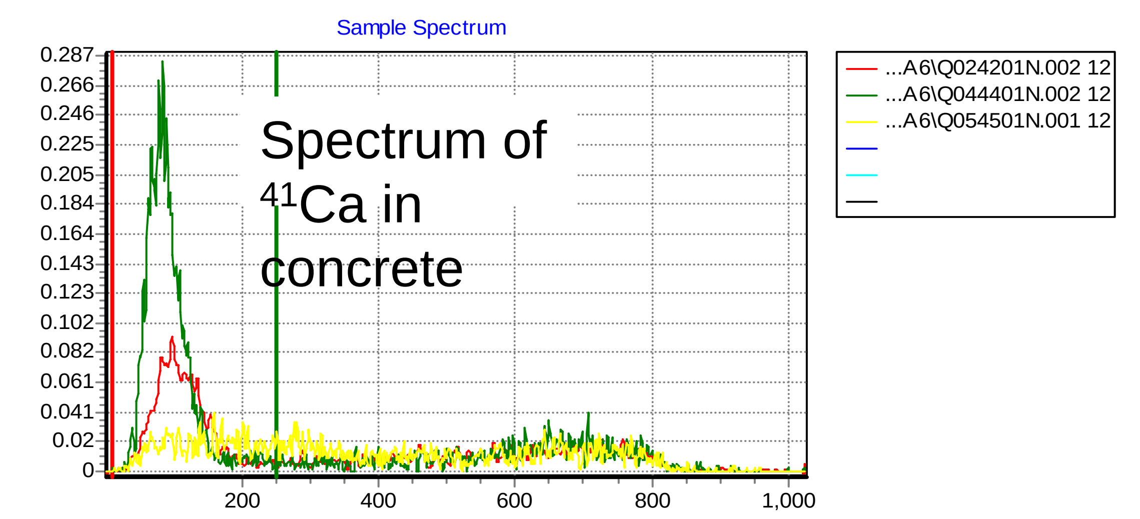
Separation of Ca from Sr and Ba by 3 repeated steps of $Ca(OH)_2$ precipitations at different NaOH concentrations

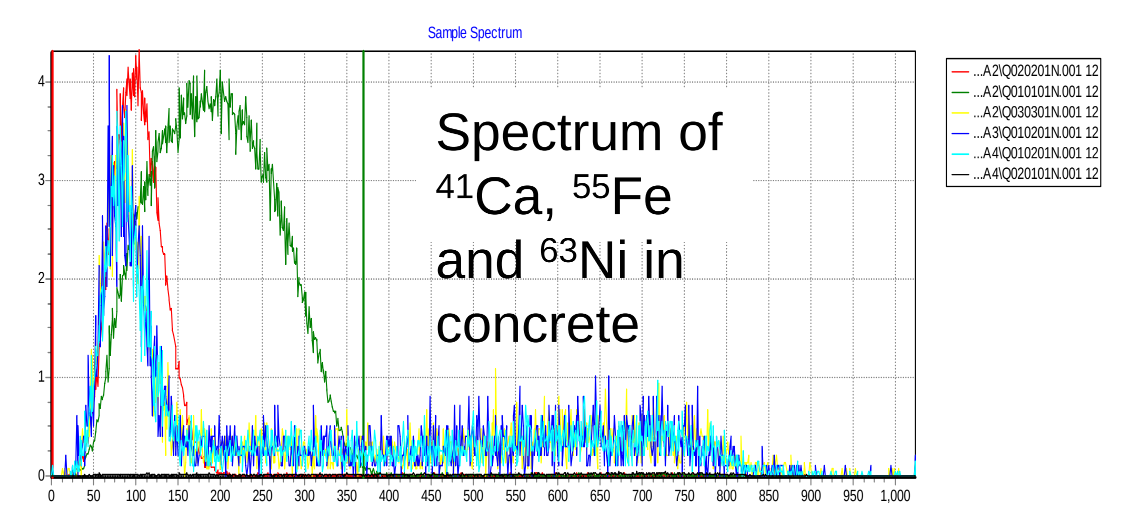
[NaOH]	Decontamination factor, 3 precipitations		Recovery of Ca, %		
mol/l	Ba	Sr	1 prec.	2 prec	3 prec
0.10	6.54×10^4	6.54×10^4	54.80	39.20	22.40
0.15	6.33×10^4	5.17×10^4	66.00	56.00	33.20
0.20	5.37×10^4	4.97×10^4	76.00	64.00	54.00
0.30	5.01×10^4	4.57×10^4	94.00	86.00	81.20
0.40	4.62×10^4	4.47×10^4	95.20	94.80	86.00
0.50	4.71×10^4	4.42×10^4	98.00	95.20	88.00
0.60	4.71×10^4	4.37×10^4	97.60	95.60	88.40
0.80	4.51×10^4	4.10×10^4	98.00	96.20	89.20
1.50	4.19×10^4	3.77×10^4	99.94	96.60	88.40
2.00	3.81×10^4	3.18×10^4	99.35	97.20	90.00

Procedure for simultaneous determination of ^{41}Ca

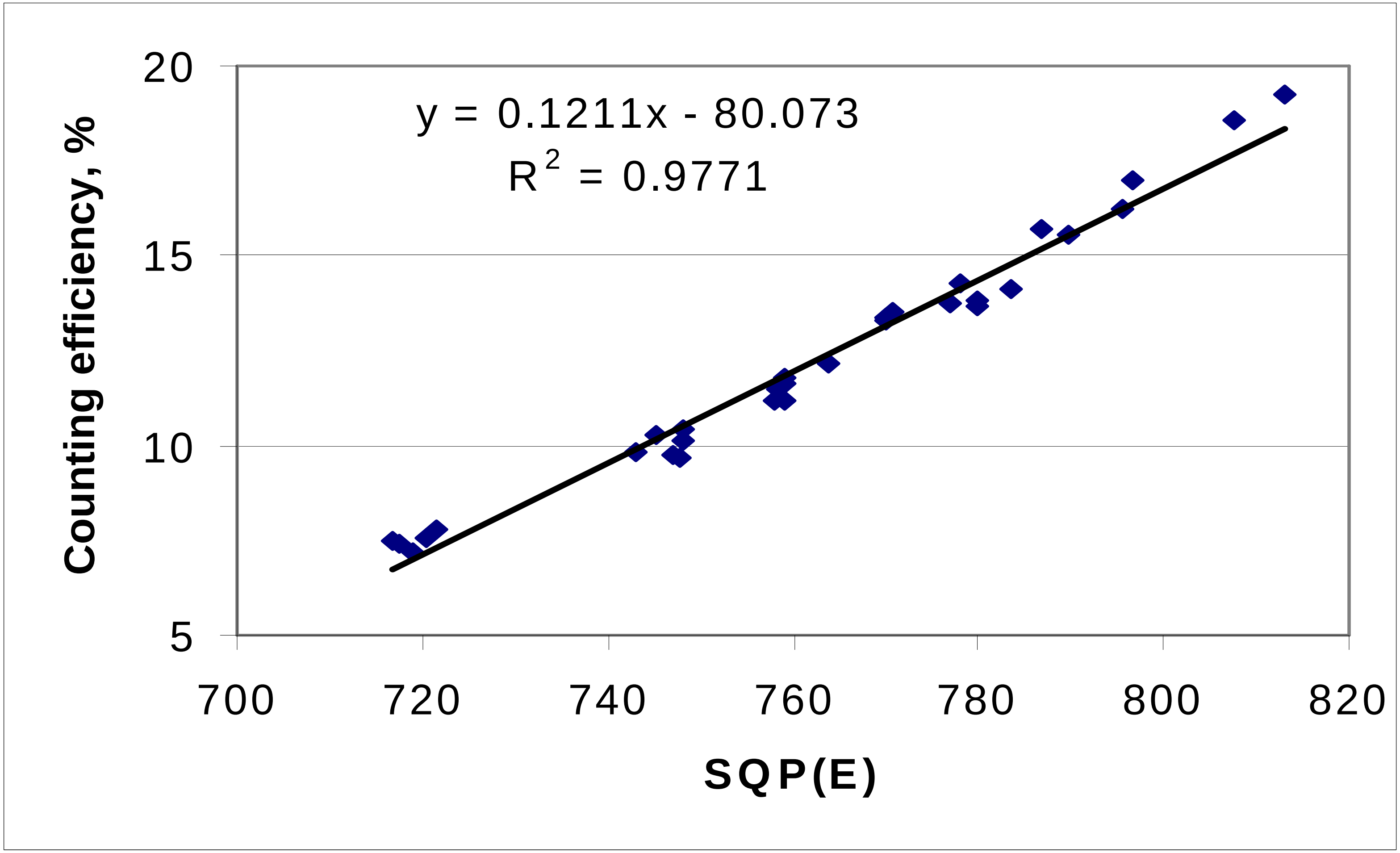


Spectra of ^{41}Ca in heavy concrete from DR-2





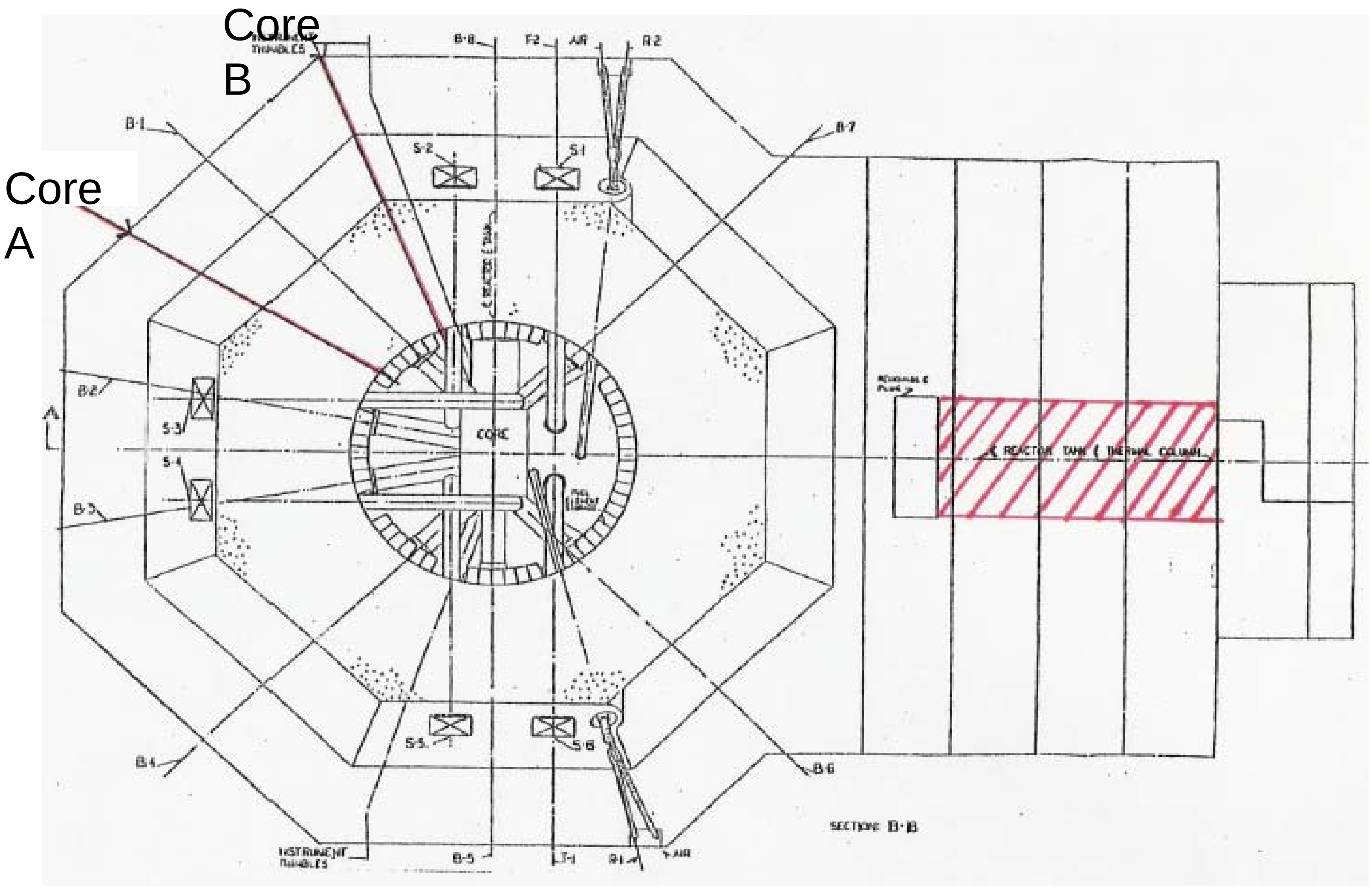
Quench correction for LSC of ^{41}Ca



Features of Method for ^{41}Ca

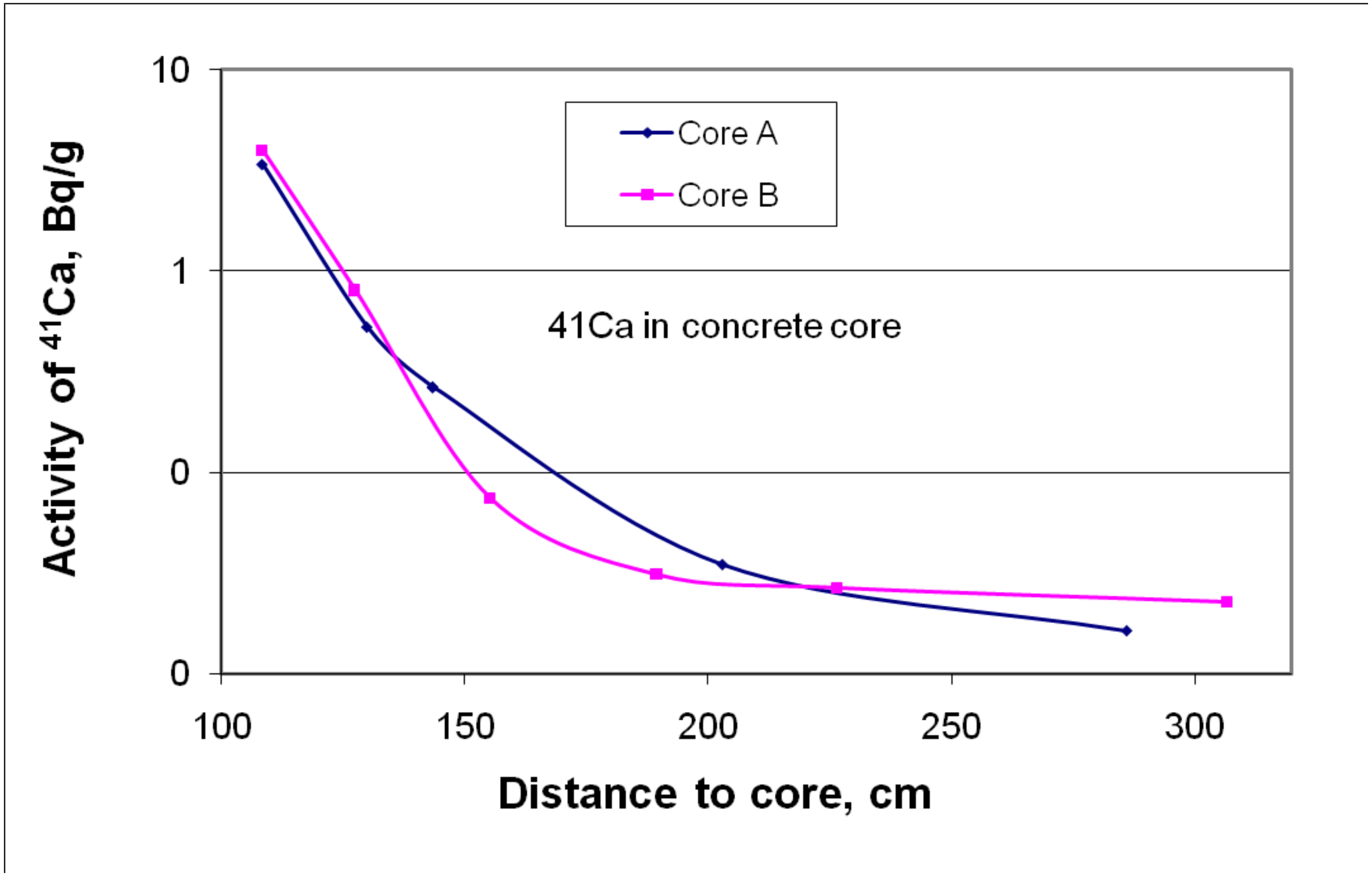
- A separation of ^{41}Ca from concrete is easy to operate
- Good decontamination from interferring radionuclides (>10^4)
- The chemical yields of the separation procedures for ^{41}Ca is 80-90%.
- The detection limits for ^{41}Ca is 0.020 Bq.

Hou X.L., Radiochim Acta, 2005



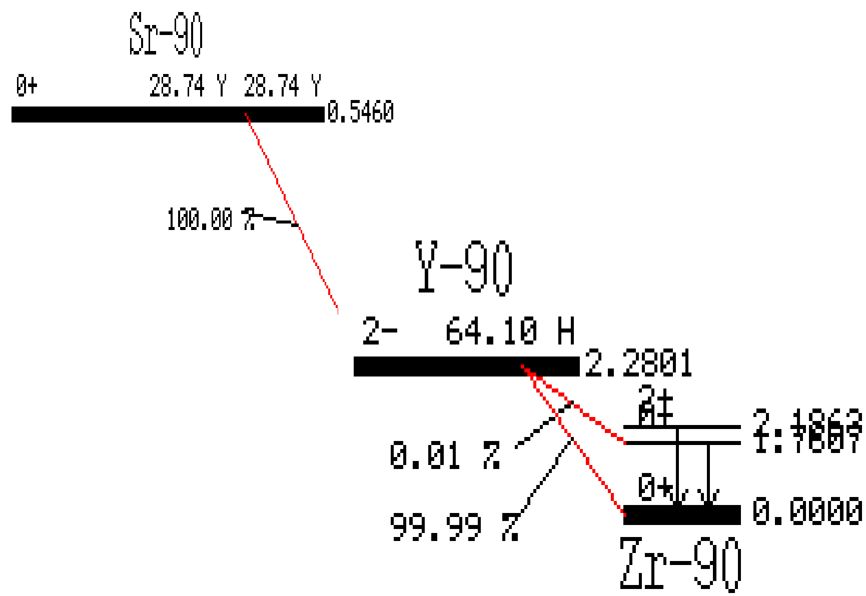
Sampling of concrete and graphite from danish reactor, DR-2

Results of ^{41}Ca in concrete from Danish reactor, DR-2



^{90}Sr in water, graphite, resin, concrete

- One of main fission products (Y=5.8%)
- Beta emitter, measured by GM detector or LSC.
- It has to be separated from other radionuclides before measurement.
- For some waste, it may contain ^{89}Sr (50.5 d), it can be also measured by LSC with ^{90}Sr.



Analytical Procedure for ^{90}Sr

Sample

Carbonate precipitate from water | Ash and Acid leaching from solid sample

Decomposed sample or Coprecipitate

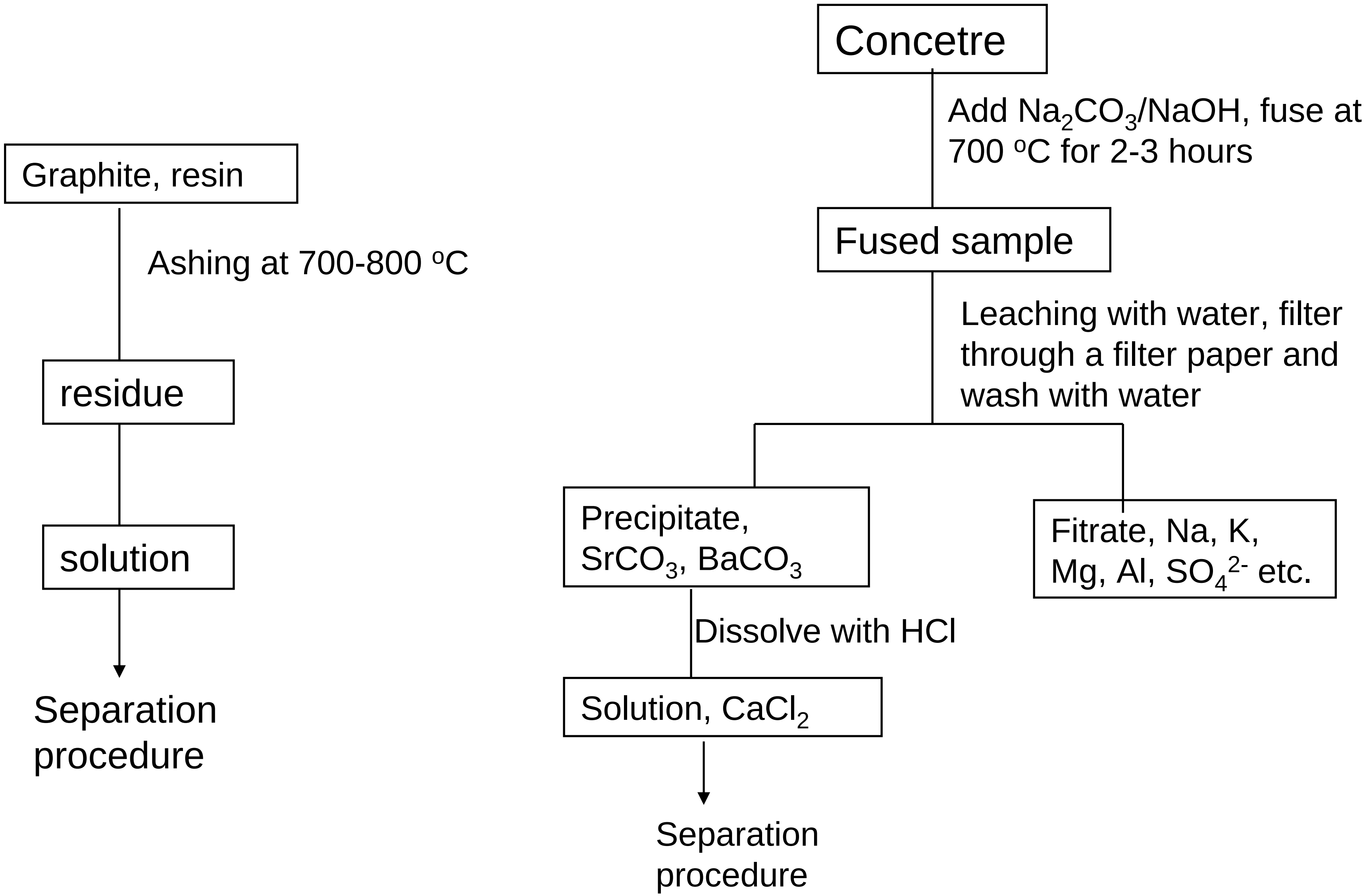
Separation of Sr from Ca, Cs, metals and transuranics

Separation of Sr from Ra and Ba

Measurement of $^{89}Sr+^{90}Sr$

Measure ^{89}Sr by Cherenkov radiation

Decomposition of solid sample



Method for the Separation of Sr

- solvent extraction
- liquid membrane extraction
- extraction chromatography (Sr-Spec resin)
- ion-exchange chromatography
- strontium rhodizonate precipitation
- $Sr(NO_3)_2$ precipitation in 70% HNO_3

  (can be used for separation of Sr from a large amount of Ca)

Solubilities of Ca, Sr, Y Ba and Ra compounds

$Ca(OH)_2$: insoluble, Ksp = 5.2 × 10^{-6}

$Sr(OH)_2$: Soluble in alkine solution

- **$SrCl_2$, $BaCl_2$ and $RaCl_2$: soluble in water**
- **$SrCl_2$: soluble in HCl<9.5 mol/L solution**
- **$BaCl_2$ and $RaCl_2$: insoluble in HCl >9 mol/l**

$Y_2(SO_4)_3$: soluble in water

$Sr(Ba, Ra)SO_4$: insoluble in water

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The new method for the separation of Sr

Separation of Sr from Ca:

$Ca(OH)_2$ precipitation

Separation of Sr from Ba and Ra

$Ba(Ra)Cl_2$ precipitation in concentrated HCl solution

Separation of ^{90}Y from Sr, Ra and Ba

$Sr(Ra, Ba)SO_4$ precipiatation

Sepation of Sr from Ca by $Ca(OH)_2$

^{85}Sr added (Bq)	Ca added (g)	^{85}Sr (Bq)		Recovery of Sr (%)	Ca in supernatant (g)	Ca decontamination (%)
		Precip.	Supern.			
1050	50.00	31.6	1058.4	97.0	0.18	99.5
1050	31.00	38.1	1037.7	96.4	0.14	99.5
1050	10.00	30.6	1029.6	97.1	0.07	99.3

* Concentration of NaOH in the solution: 0.5 mol/L

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Separation of Sr from Ba by $BaCl_2$ and $BaCrO_4$

[HCl], mol/l	Tracers added (Bq)		Supernat. ^{133}Ba (Bq) *	Precipitate ^{85}Sr (Bq) *	Recovery of Sr, %	Decontam. of Ba, %
	^{85}Sr	^{133}Ba				
8.5	1050	1510	918.8±14.2	2.0±3.4	99.8±0.3	40.0±1.3
9.0	1050	1510	484.7±18.4	2.1±2.4	98.8±0.3	67.9±1.8
9.5	1050	1510	43.8±9.4	62.4±5.9	94.1±0.6	97.1±1.4
10.0	1050	1510	40.5±7.2	331.2±11.1	68.5±1.5	97.3±1.3
10.5	1050	1510	28.6±4.2	743.4±18.4	29.5±1.3	98.1±2.7
11.0	1050	1510	7.9±4.8	846.3±21.2	21.1±1.1	99.5±1.3
$BaCrO_4$	1050	1510	15.3±5.7	49.0±7.8	95.3±0.7	99.0±0.4

* Average and standard deviation of two determinations

Separation of Y from Ra, Sr, and Ba by sulphate precipitation

Tracer	Added	Supernat.	Precipitate	Recovery of Y, %	Decontam.of Sr, Ba, Ra %
Y, mg	11.10	10.95±0.22		98.6±2.0	
^{85}Sr, Bq	1050	8.7±2.4	1042±38		99.2±0.2
^{133}Ba, Bq	1510	2.2±1.8	1511±21		99.9±0.1
^{226}Ra, Bq	33.0	0.14±0.26	32.87±0.47		99.6±1.4

Separation procedure of ^{90}Sr

Solution

Add ^{85}Sr, $SrCl_2$, pH8-10,add $(NH_4)_2CO_3$, stand overnight

Supernatant

Precipitate ($SrCO_3$), Ca, Ra, Ba, transit metals, transuanics

Add HNO_3 to disolve, Fe^{3+}, add NaOH to 0.5 mol/L, centrifuge

Precipitate ($Ca(OH)_2$, Fe, transuranics

Supernatant, Sr

Add HNO_3, Y, Sr and Ba, 3 weeks ingrowth of ^{90}Y, add H_2SO_4, centrofuge

Precipitate ($(Sr, Ba, Ra)SO_4$

Supernatant, Y-90

Add $H_2C_2O_4$, centrofuge

Precipitate, $Y_2(C_2O_4)_3$ H_2O → β Meaurement of Y-90, calculation of Sr-90

Chen, Hou, Nielsen, Dahlgaard, Yu, *Anal. Chim. Actc*, 466 (1): 109-116, 2002

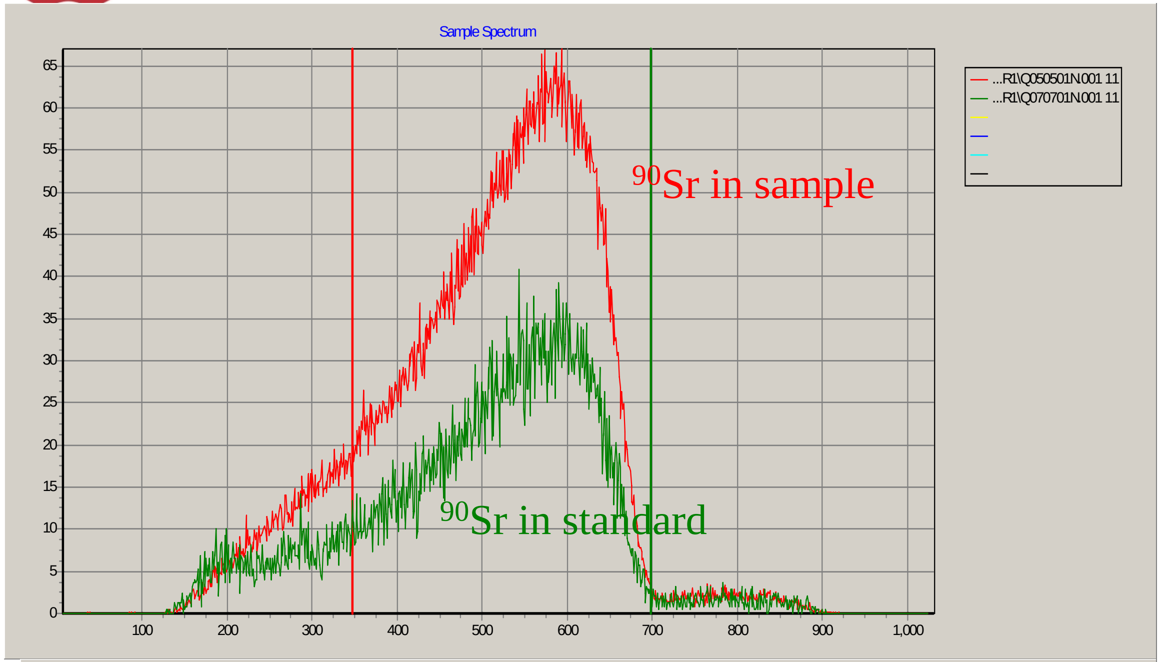


Fig.1 Beta spectrum of Sr sample separated from DR1 sample

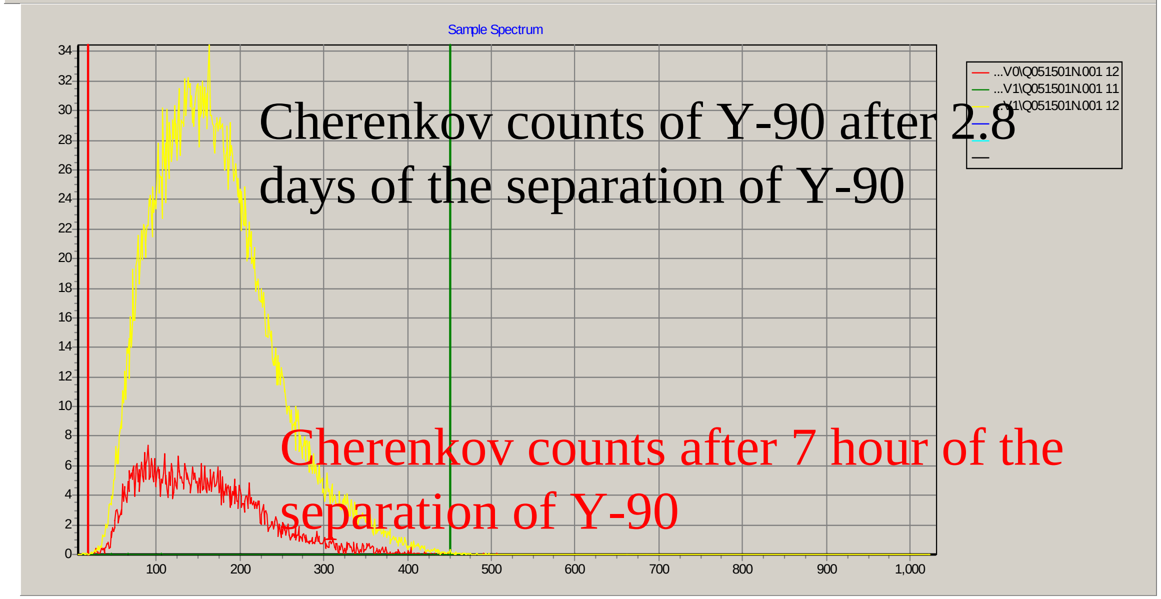
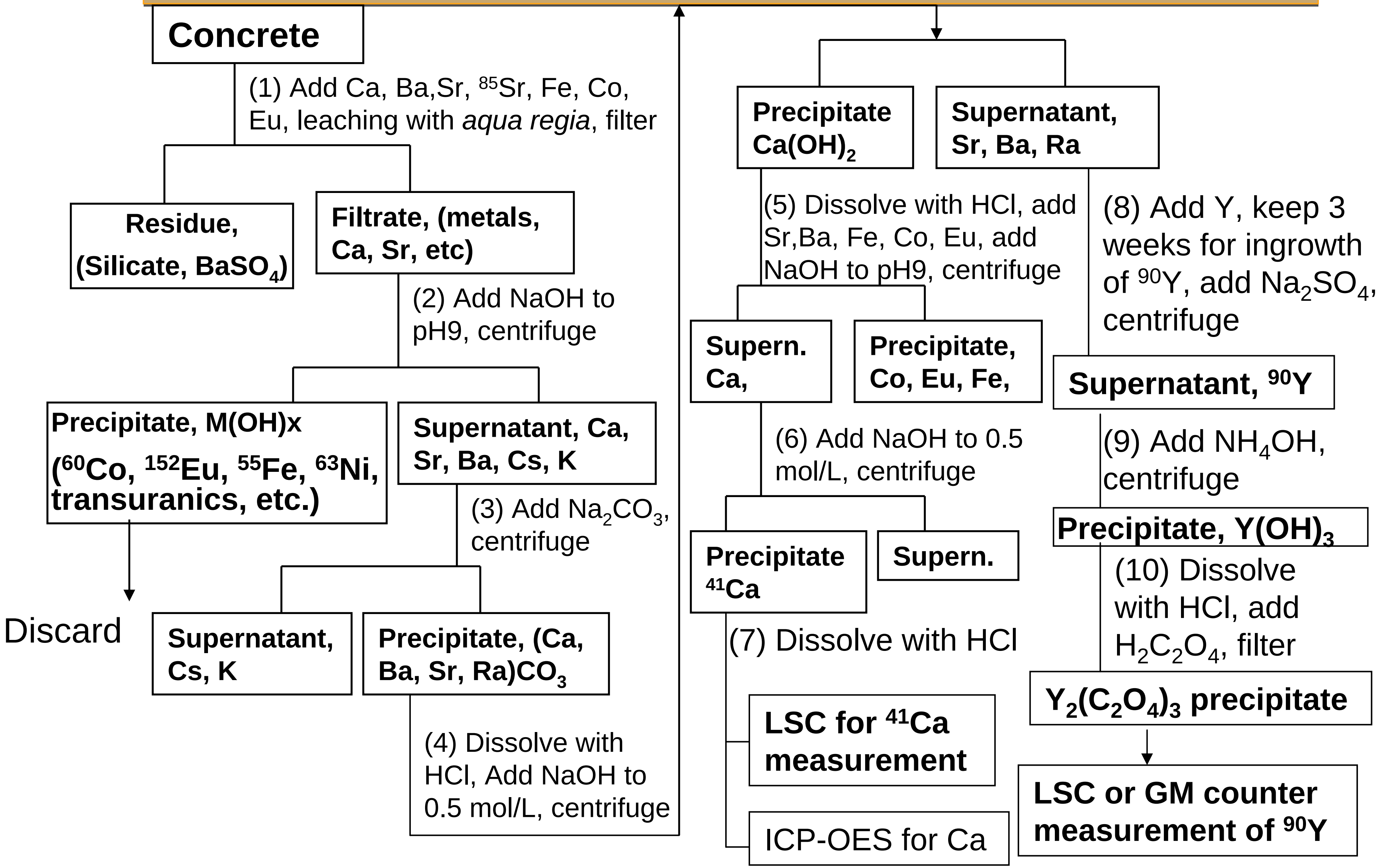


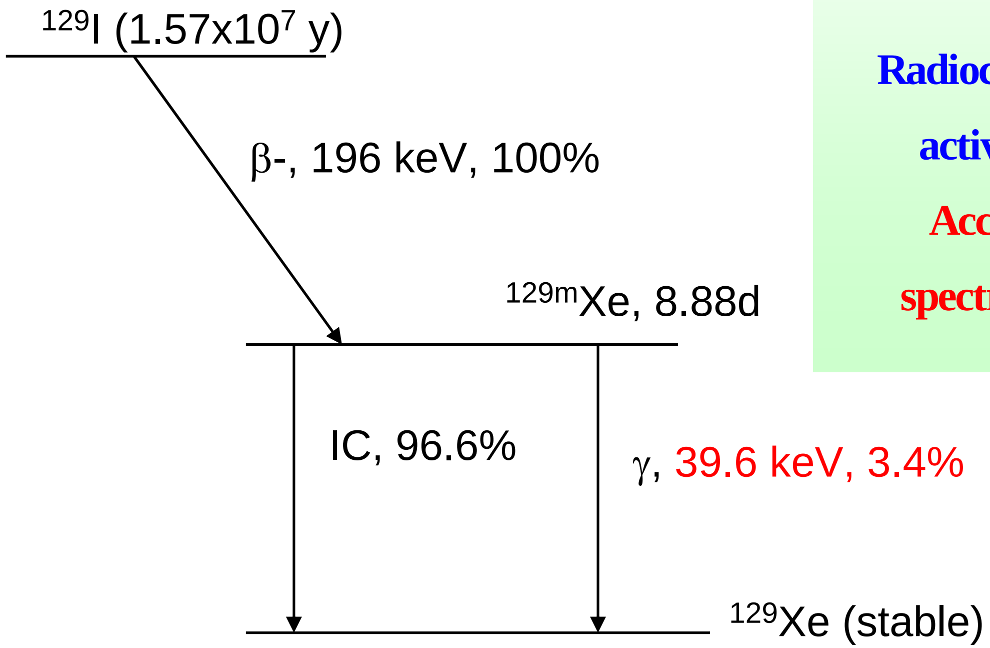
Fig.2 Cherenkov radiation of Sr sample separated from one DR1 sample

Combined procedure for simultaneous determination of ^{41}Ca and ^{90}Sr



Analytical Method for ^{129}I and their detection limits

Method	Detection limit (atoms)
Liquid scintillation	10^{12} (1 mBq)
γ-spectrometry	10^{14} (0.1 Bq)
ICP-MS	5×10^{11}
Radiochemical neutron activation analysis	10^{8}
Accelerator mass spectrometry (AMS)	10^{6}



Separation procedure of iodine in solid samples

Solid samples

↓ *decompose sample by combustion, acid digestion, or alkali fusion*

solution

↓ Extracting with CCl_4, Back-extracting with H_2SO_3, repeat

Iodide separated → Measurement by LSC

↓ convert to MgI_2 or AgI

Iodine Sample → Gamma measurement / AMS

↓

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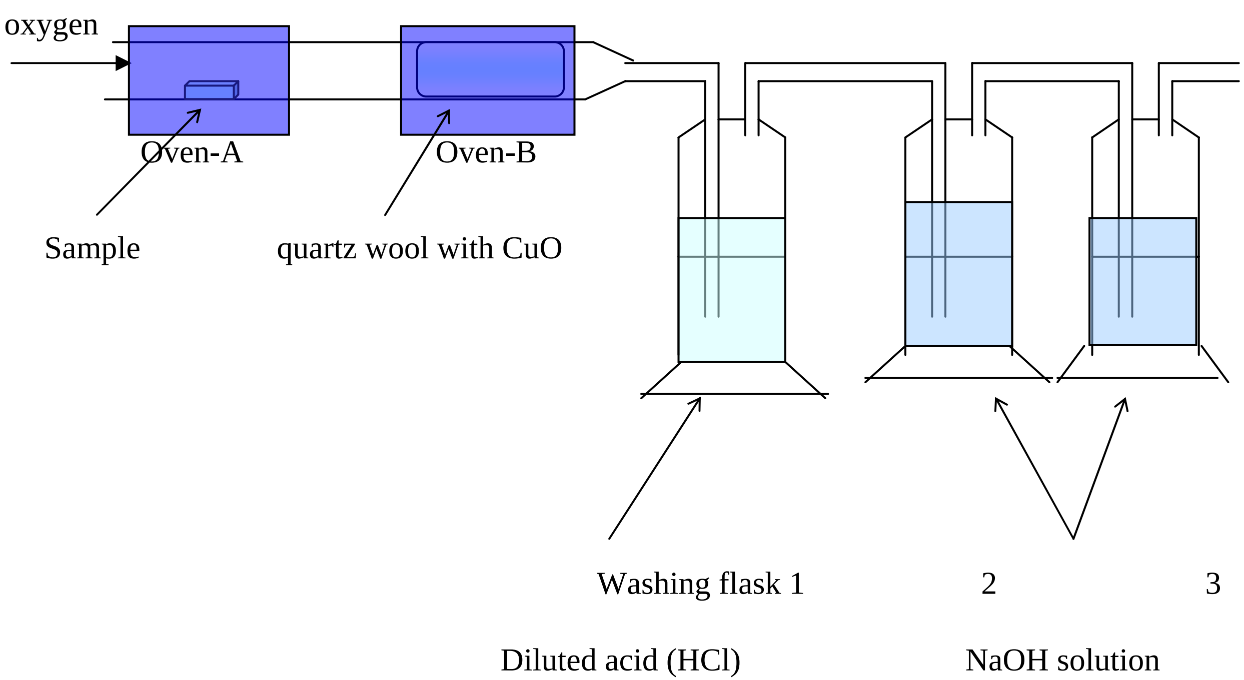
Separation of ^{129}I from soild waste by combustion method

- Flask 1: ^{3}H, ^{129}I, ^{99}Tc
- Flask 2,3: ^{14}C, ^{129}I



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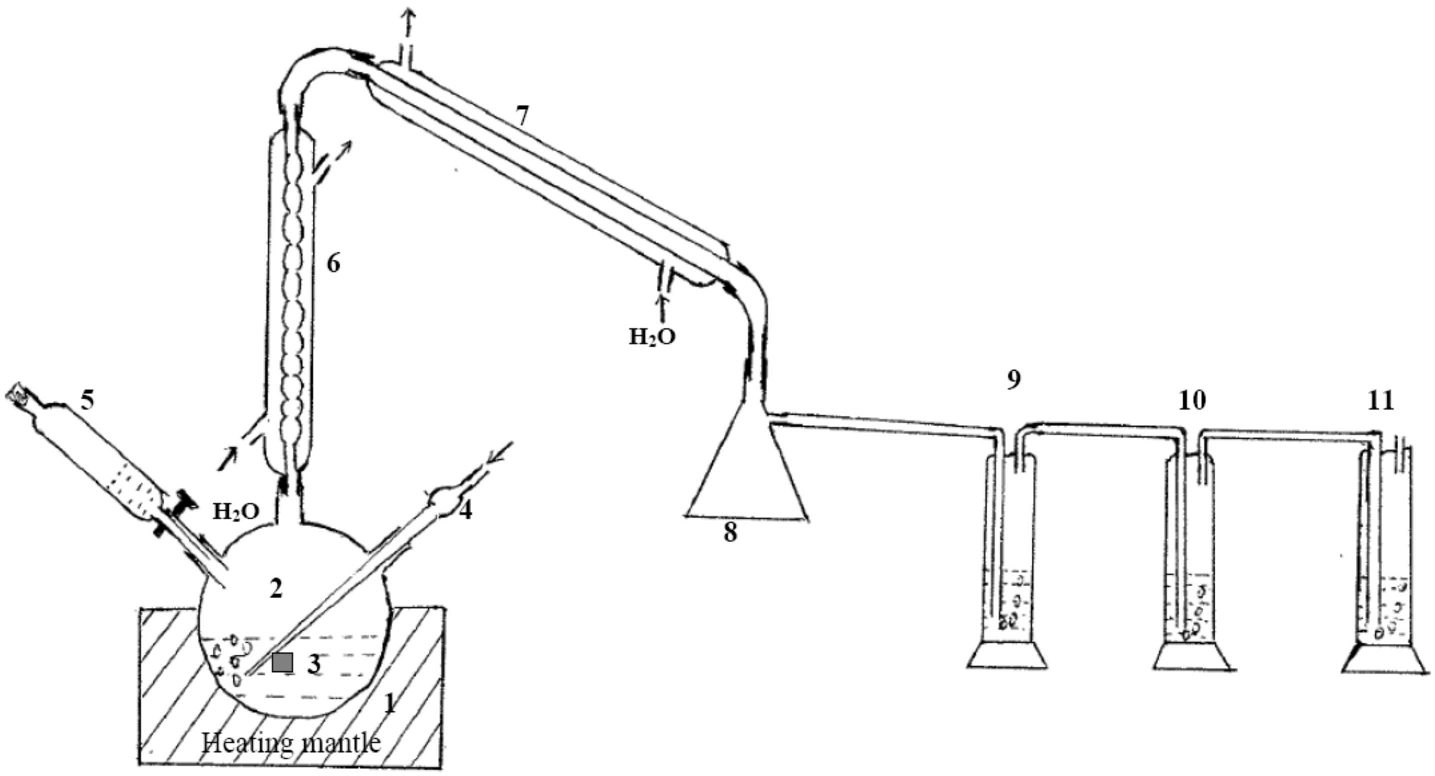
Schematic diagram of acid digestion system of for separation of ^{36}Cl and ^{129}I



1-Heating mantle; 2-three-necked flask; 3-sample in acid mixture; 4-bubbling tube; 5-separating funnel for adding acids; 6,7-reflux condenser; 8-receiver; 9-wash bottle containing water; 10, 11-absorption bottles containing 0.4 mol/l NaOH

Separation of ^{129}I from soild waste by Alkali fusion

Solid samples (concrete)

↓ add $NaOH/Na_2CO_3$, iodine carrier, fusion at 600°C for 2 h

Fusee cake

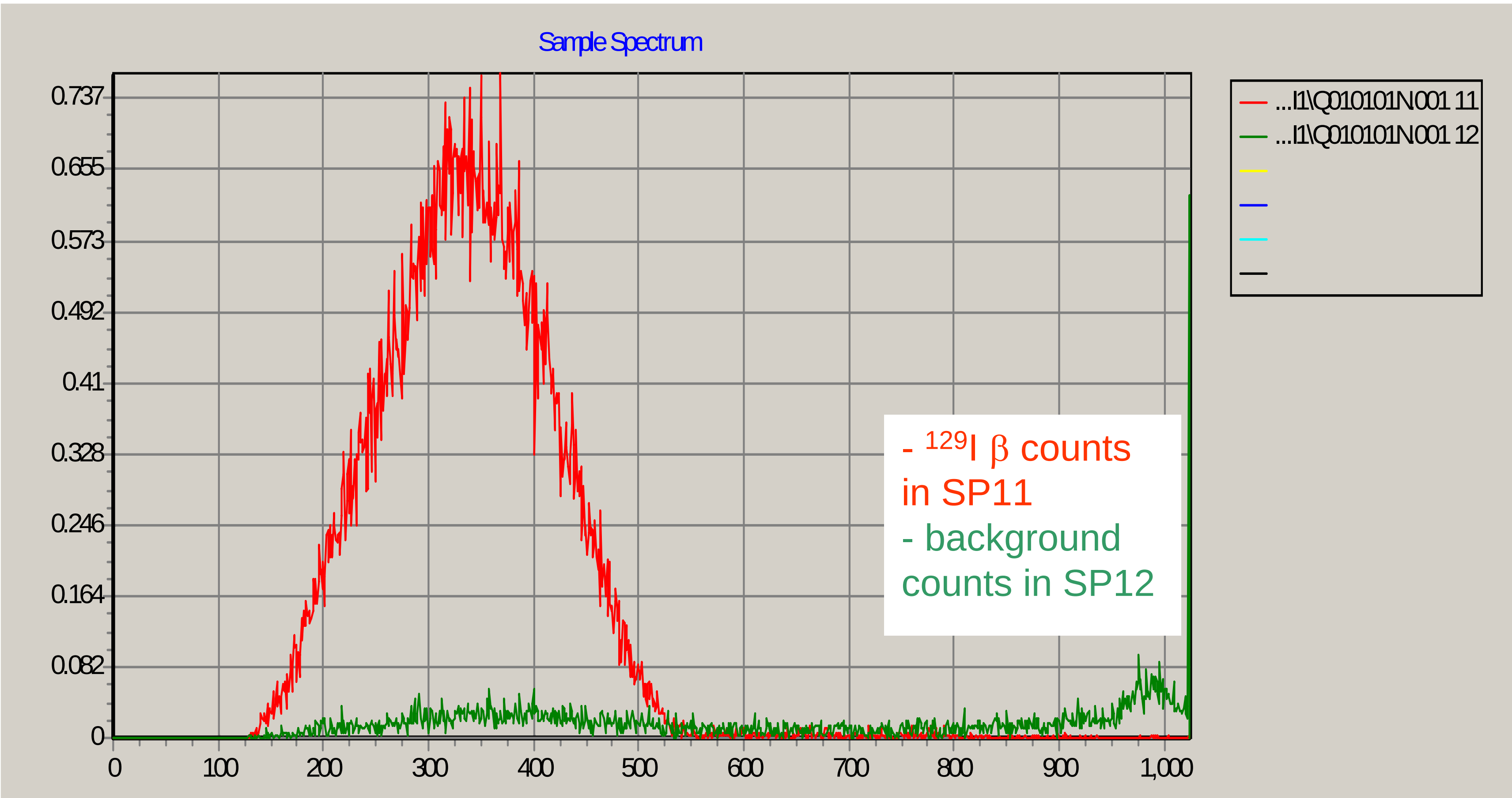
↓ Leaching with H2O, filter to remove residue (precipitation)

Solution with ^{129}I

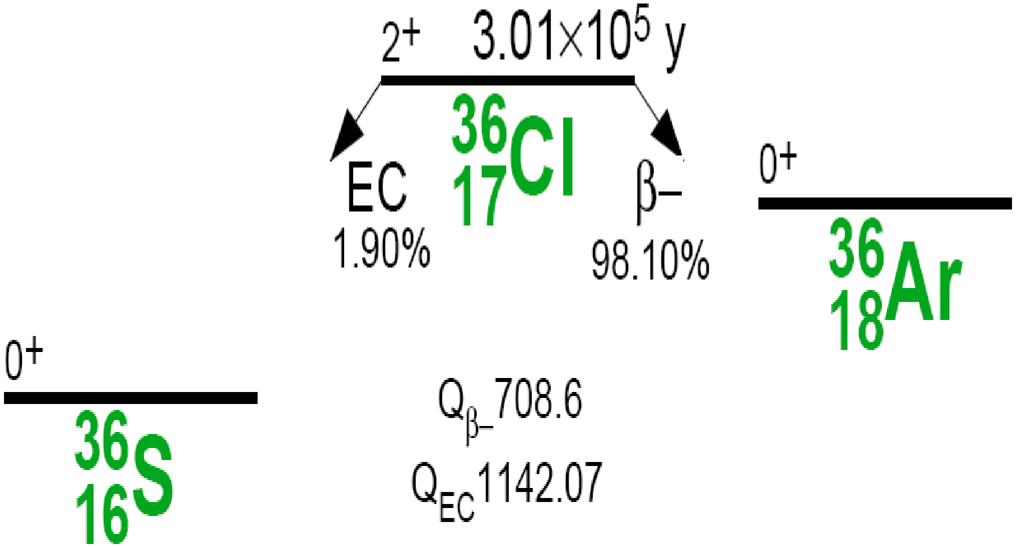
↓ Convert iodine to iodide, extract with CCl_4, abck extract with NaSO3

Separated Iodine

Beta spectrum of ^{129}I by LSC



Determination of ^{36}Cl



- ^{36}Cl is long-lived radionuclides (3x10^{5} yrs)
- ^{36}Cl decays mainly by pure beta emission of Emax=708.6 keV.
- ^{36}Cl measurement is normally carried out by LSC and AMS

Determination of ^{36}Cl and ^{129}I in graphite --- Sample decomposition

- Ashing at 900°C: ---iodine and part of Cl are lost.

- Decomposition at 900°C with O_2 and trapping iodine in NaOH solution: ---good recovery for iodine, but not good for chlorine

- Leaching with acid (HNO_3) at heating: --- not complete remove iodine and Cl from graphite, and loss of the leached iodine.

- Digestion with HNO_3 and trapping iodine and chlorine with NaOH: ---- Not complete removal of iodine and chlorine

- How to Do?

Determination of ^{36}Cl and ^{129}I in graphite --- Sample decomposition

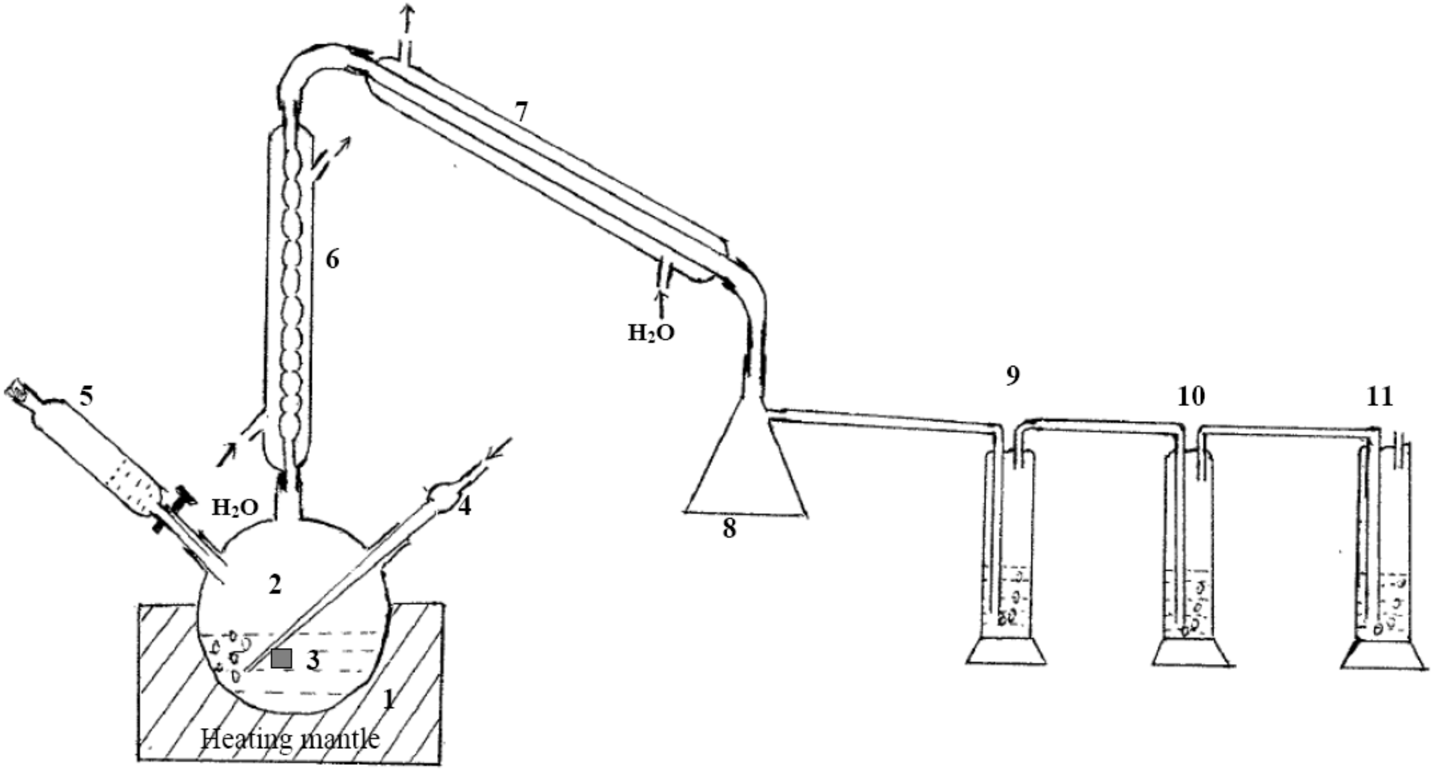
- Graphite can be completely dissolved in a mixture of acids: HNO_3+H_2SO_4 +$HClO_4$

- The optima ratio of mixture is:

$$H_2SO_4:HNO_3:HClO_4 =15:4.1$$

- A closed dissolution system is used for dissolve graphite in heating, Cl on the condenser tube and trap solution, while iodine mainly in the trap solution.

Schematic diagram of dissolution system of graphite for determination of ^{36}Cl and ^{129}I



1-Heating mantle; 2-three-necked flask; 3-sample in acid mixture; 4-bubbling tube; 5-separating funnel for adding acids; 6,7-reflux condenser; 8-receiver; 9-wash bottle containing water; 10, 11-absorption bottles containing 0.4 mol/l NaOH

Determination of ^{36}Cl and ^{129}I in concrete --- Sample decomposition

- Leaching with acid (HNO_3) at heating: --- not complete remove iodine and Cl from graphite, and loss of the leached iodine.

- Digestion with HNO_3 and trapping iodine and chlorine with NaOH: ---- Not complete removal of iodine and chlorine

- Alklinal fussion using NaOH and Na_2CO_3, dissolution of fused cake in water, the supernatant is used for ^{129}I and ^{36}Cl: ---- sample is completely decomposed and iodine and Cl are released. Iodine and Cl are not lost in alkaline medium

Determination of ^{36}Cl and ^{129}I in stainless steel --- Sample decomposition

- Stainless steel is normally dissolved with HCl or HCl+HNO3: --- could not be used for ^{36}Cl because of too much Cl in HCl is introduced.

- Single acid, HNO_3, could not dissolve stainless steel.

- 10M H_2SO_4 with H_3PO_4 is sucessfully used for dissolve stainless steel for ^{129}I and ^{36}Cl: ---- sample is completely decomposed and iodine and Cl are released.

Separation of Cl from matrices and other radionuclides

- ✓ Specific precipitation of Cl^- with Ag^+ (AgCl) can be used to selectively separation of Cl from matrix and other radionuclides (except iodine and bromine).

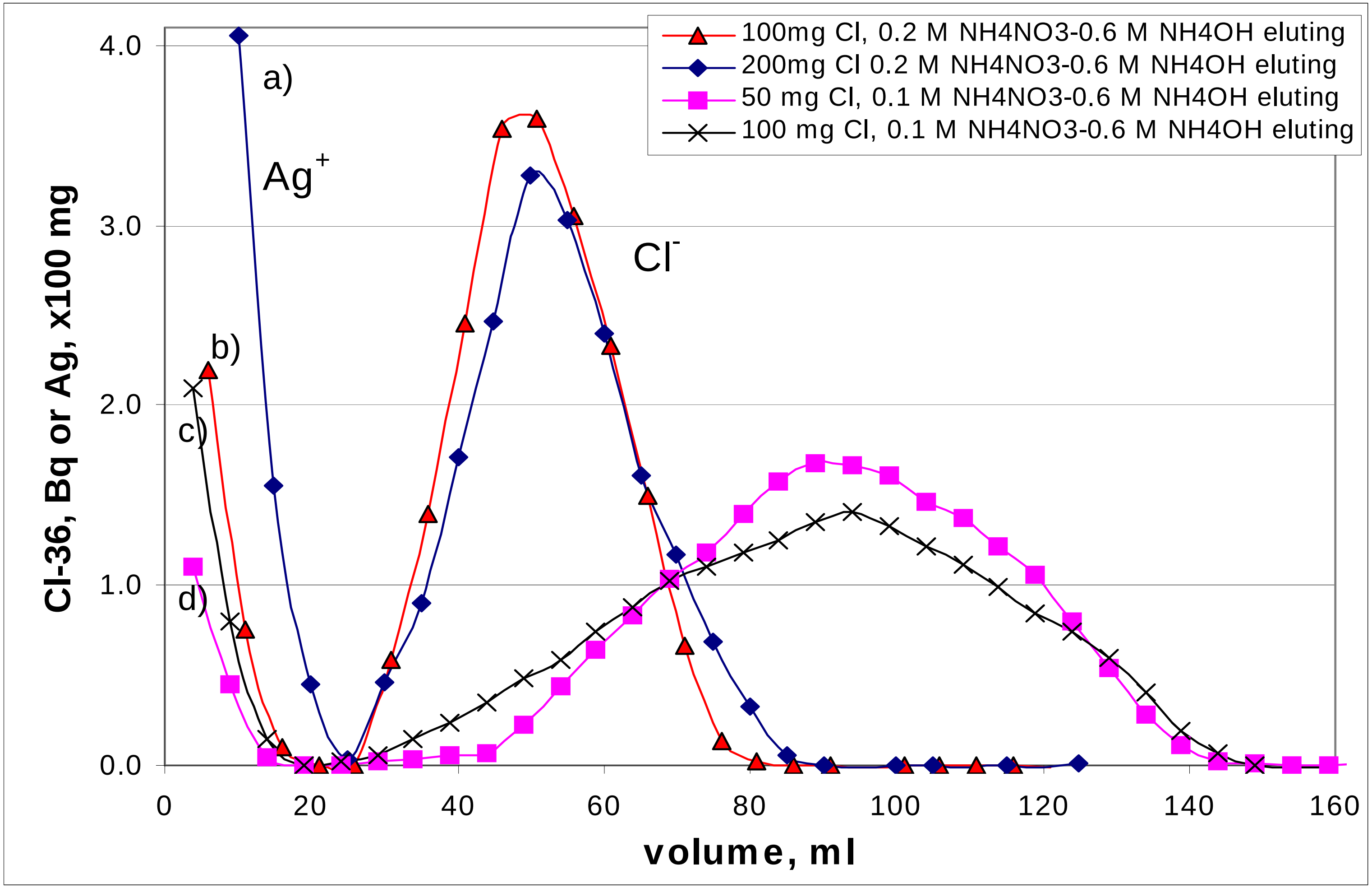
- ✓ Iodine (^{129}I) should be first separated from the solution before AgCl precipitation.

- ✓ ^{129}I can be separated by solvent extraction using $CHCl_3$

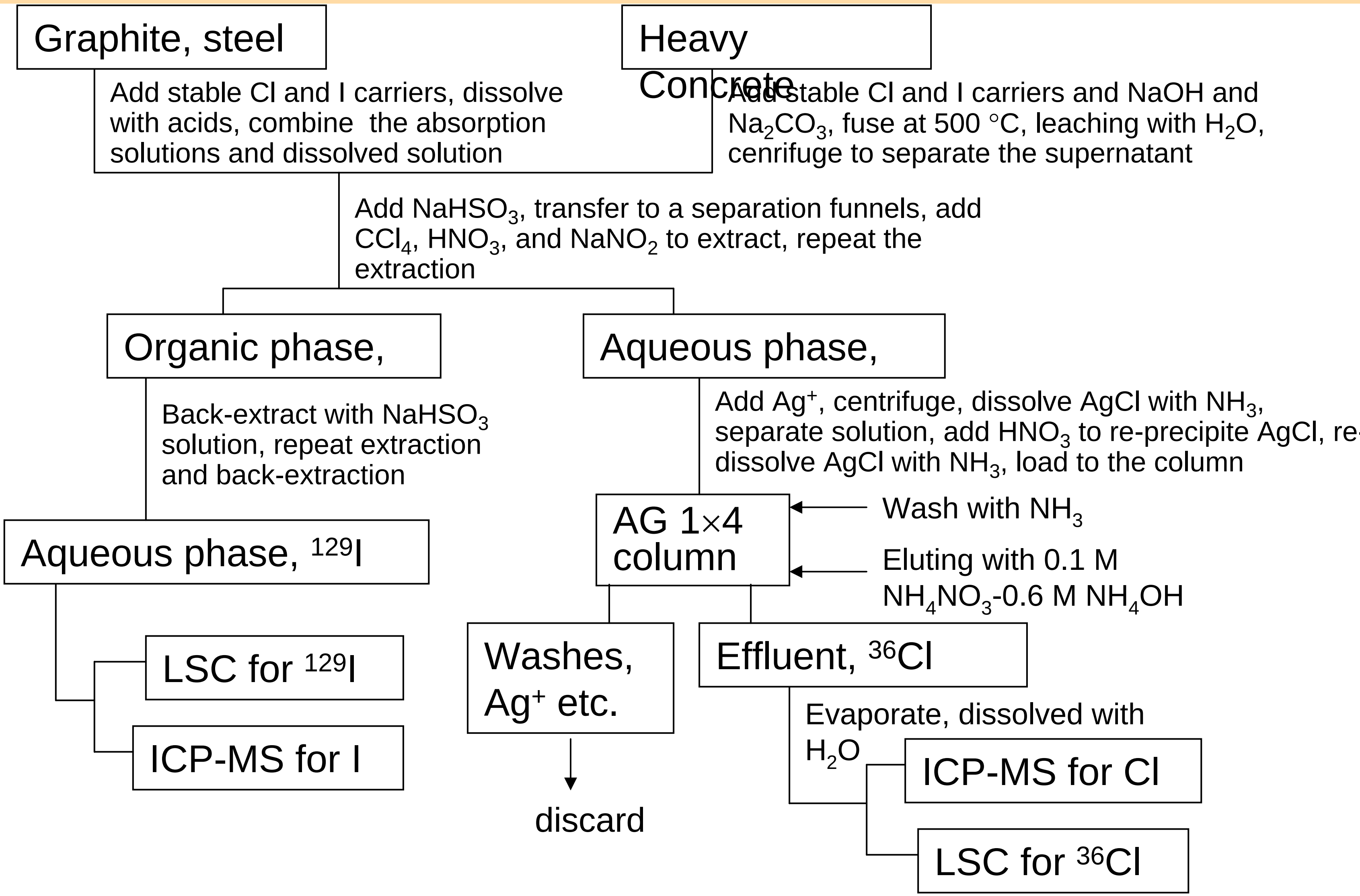
- ✓ No need to separate Br, since no long-lived radioisotopes of Br in the waste and environmental samples.

- ✓ The separated AgCl can be dissolved in NH_4OH and mixed with scintillation cocktail for LSC: But less AgCl can be used and high quench effect. How to improve?

Separation of Ag^+ and Cl^- in anion exchange chromatography



Combined Analytical procedure for ^{36}Cl and ^{129}I



Hou et al., Anal. Chem., 2007

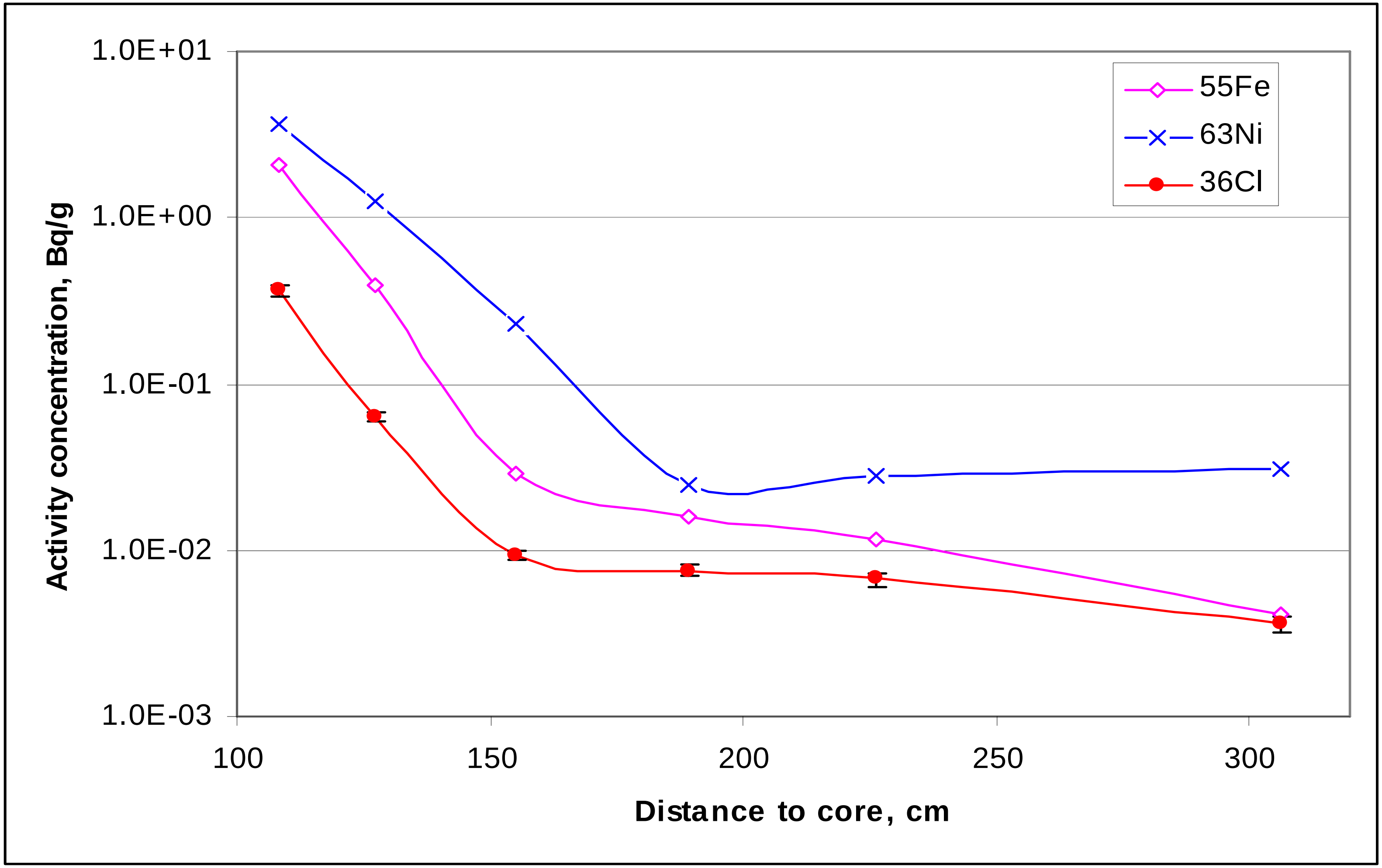
Recovery of Cl and decontamination factors for other elements and radionuclides in the chemical separation procedure

Element	AgCl precipitation	Anion exchange	Whole procedure
Cl (recovery, %)	96.5	98.3	94.7 ± 3.2
I (^{125}I)	1.4×10^3	5.4×10^3	2.9×10^6
S	1.5×10^3		5.6×10^6
tritium	2.1×10^3		4.8×10^6
^{14}C (CO_3^{2-})	1.5×10^3		2.8×10^6
Co (^{60}Co)	1.9×10^3	8.5×10^3	8.5×10^6
Eu (^{152}Eu)	4.7×10^3	6.5×10^3	9.9×10^6
Cs (^{137}Cs)	3.8×10^3	5.1×10^3	7.9×10^6
Ba (^{133}Ba)	6.7×10^3	4.9×10^3	5.6×10^6
Sr (^{85}Sr)	4.7×10^3	8.3×10^3	8.7×10^6
Ni (^{63}Ni)	5.9×10^3	9.8×10^3	9.8×10^6
Fe (^{55}Fe)	1.9×10^3	8.8×10^3	8.1×10^6

Performance of the procedure for ^{36}Cl

- Recovery of Cl: >70%
- Decontamination factors for most of radionculides: $>10^6$
- Detection limit using LSC : 14 mBq
- Decommissioing samples, concrete, graphite, stainless steel, aluminum, lead, have been sucessfully analysed for ^{36}Cl

Distribution of ^{36}Cl in the concrete core from Danish research reactor DR-2 with comparison to ^{55}Fe, and ^{63}Ni



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Concentrations of ^{36}Cl in samples from the graphite thermal column, aluminum tanks and lead shielding in the concrete core from DR-2 reactor

Sample	Code	^{36}Cl, Bq/g mean±SD	^{63}Ni, Bq/g	$^{36}Cl/^{63}Ni$ Activity ratio
Graphite	5.5 Yi	0.18±0.03	5.76	0.030
Graphite	5.5 Yy	3.58±0.13	102	0.035
Graphite	5.5 Ii	22.6±1.5	499	0.045
Graphite	5.5 Iy	6.61±0.52	74.9	0.088
Graphite	7.5 Yi	6.37±0.48	134	0.048
Graphite	7.5 Yy	5.57±0.54	88.3	0.063
Graphite	7.5 Ii	39.9±3.4	758	0.053
Graphite	G	3.33±0.28	61.2	0.054
Aluminum	B1	0.027±0.003	15.6	0.0017
Aluminum	B2	0.023±0.03	15.5	0.0015
lead	B4	0.0032±0.0012	2.58	0.0012

Combined analytical procedure for ^{36}Cl, ^{129}I, ^{41}Ca, ^{63}Ni and ^{55}Fe